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(54) **Use of titanium and zirconium compounds as homogeneous catalyst and novel titanium and zirconium compounds.**

(57) The use of chelating bisphenoxide and binaphtoxide titanium and zirconium compounds as homogeneous catalysts in the polymerization and oligomerization of unsaturated hydrocarbons, in particular the polymerizations of olefinically unsaturated compounds and the cyclic trimerization of terminal acetylenes, is described.

Furthermore, certain novel chelating silyl containing binaphtoxide titanium and zirconium compounds are described.

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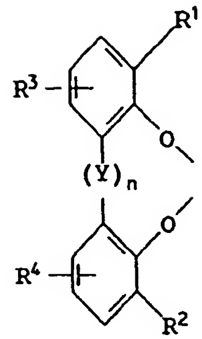

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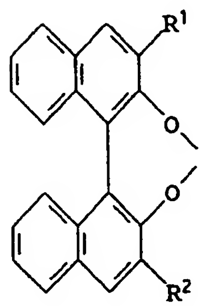


(III)

wherein:

- R^1 and R^2 independently represent a sterically hindering alkyl group or an alkoxy group of general formula OR' with R' as previously defined, or a silyl group of general formula $SiR^aR^bR^c$ with R^a, R^b and R^c independently representing a lower alkyl group, an aryl group, an arylalkyl group or an alkylaryl group;
- R^3 and R^4 independently represent hydrogen, an optionally substituted aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms, a silyl group or an alkoxy group of general formula OR' with R' as previously defined;
- Y is a divalent bridging group selected from the group consisting of methylene, ethylene, -S- and -O-; and
- n is 0 or 1.

The said homogeneous catalysts are particularly useful in the polymerization or oligomerization of ethene, propene or hexene, while the best results are achieved in the polymerization or oligomerization of ethene. The term "olefinically unsaturated hydrocarbon" wherever used in this specification should be interpreted wide enough as to comprise both mono-unsaturated compounds as well as diolefinically unsaturated compounds. From the latter group of compounds 1,3-butadiene can be cited as example. The mono-olefins can have terminal unsaturation (alpha-olefins) or internal unsaturation as in e.g. 2-hexene or 3-hexene.

On the other hand, the said titanium and zirconium compounds may also be effectively used as homogeneous catalysts in the oligomerization of terminal acetylenes and more particularly in the cyclic trimerization of terminal acetylenes. Preferably, said acetylenes have the general formula (IV):

$$H\text{-}C{\equiv}C\text{-}R \qquad (IV)$$

wherein R represents a hydrocarbyl silyl group, an optionally substituted aryl group or an alkyl group of 1 to 20 carbon atoms other than tertiary alkyl. In an even more preferred embodiment, said group R is selected from the group consisting of trimethyl silyl, phenyl and p-tolyl.

The polymerization or oligomerization is effected by methods known per se, it can be carried out in bulk, in solution, in slurry or in gasphase reaction. Usual temperatures will be in the range of from 95 to 150 °C, the pressure will normally range from 1 to 100 bar, preferably from 3 to 70 bar.

It is preferred that the groups X^1 and X^2 as depicted in formula (I) are the same and selected from the group consisting of halogen, alkylene trialkyl silyl, aryl, alkylaryl, arylalkyl and lower alkyl. From this group of preferred substituents chlorine, benzyl, methylene trimethyl silyl and methyl are the most preferred members.

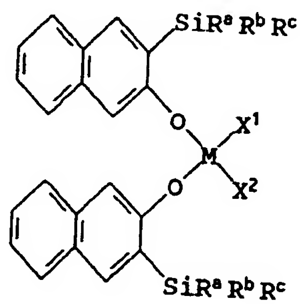
If the chelating alkoxide ligand is the one represented by general formula (II), n may be either 0 or 1, whereby in the event n equals 1, it is preferred that Y is a methylene group or -S-. In addition hereto, it is also preferred

that R^1 and R^2 are the same and represent a bulky alkyl group of 1 to 10 carbon atoms, preferably tertiary butyl. The other substituents R^3 and R^4 are preferably both located on the meta-position in relation to R^1 and R^2 respectively, while in such a case it is preferred that R^3 and R^4 are the same and represent methoxy, methyl or ethyl.

Particularly preferred are 2,2'-(4-OMe,6-$tBuC_6H_2O)_2Ti(CH_2Ph)_2$,
2,2'-S(4-Me,6-$tBuC_6H_2O)_2Ti(CH_2Ph)_2$ and
2,2'-CH_2(4-Et,6-$tBuC_6H_2O)_2Ti(CH_2Ph)_2$, whereby
2,2'-S(4-Me,6-$tBuC_6H_2O)_2Ti(CH_2Ph)_2$ is most preferred for use as olefin polymerization catalyst.

If, however, the chelating alkoxide ligand is the one represented by general formula (III), it is preferred that R^1 and R^2 both represent a silyl group of general formula $SiR^aR^bR^c$ with R^a, R^b and R^c independently representing a lower alkyl group, an aryl group, an arylalkyl group or an alkylaryl group. In such a case, it is preferred that R^1 and R^2 are selected from trimethyl silyl, diphenyl methyl silyl, triphenyl silyl and dimethyl phenyl silyl, with R^1 and R^2 preferably being the same.

The present invention also relates to novel compounds of general formula (V):



(V)

wherein:

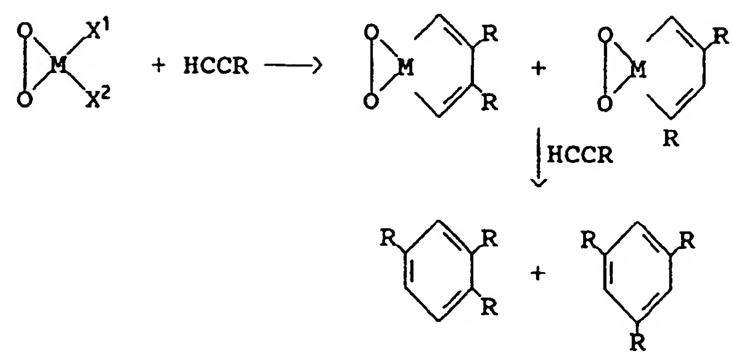
- M is Ti or Zr;
- X^1 and X^2 independently represent halogen, an optionally substituted aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms, a silyl group or an alkoxy group of general formula -OR' with R' being an aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms; and
- R^a, R^b and R^c independently represent a lower alkyl group, an aryl group, an arylalkyl group or an alkylaryl group, of which methyl and phenyl are preferred.

In a preferred embodiment of the present invention X^1 and X^2 are the same and selected from the group consisting of halogen, alkylene trialkyl silyl, aryl, alkylaryl, arylalkyl and lower alkyl, while from this group chlorine, benzyl, methylene trimethyl silyl and methyl are the most preferred members.

Preferred novel compounds are those of formula V wherein either R^a, R^b and R^c are selected from methyl and phenyl, or wherein M=Zr or Ti, R^a=R^b=R^c=independently methyl or phenyl and X^1=X^2=C1 or benzyl, or methyl, or wherein M=Zr, R^a=R^b=R^c=phenyl and X^1=X^2=methylene trimethyl silyl.

If chelating alkoxide titanium and zirconium compounds as described hereinbefore are used as homogeneous catalyst for the polymerization of olefins such as ethene and propene, a cocatalyst is required for activating the catalyst. In principle, any cocatalyst known in the art can be used, but it is preferred to use an organoalumium compound, such as diethylaluminium chloride or methylaluminoxane. The best results however, are obtained when using methylaluminoxane.

When used as catalyst in the cyclic trimerization of terminal acetylenes to yield benzenes, the catalyst needs no activation by means of a cocatalyst due to the presence of the terminal triple bond and the resulting acidic character of the terminal hydrogen atom in combination with the basic character of the bonding between the titanium or zirconium atom and the X^1 and X^2 group. This also explains why H-C≡C-tAlkyl and internal acetylenes do not undergo the cyclic trimerization reaction: H-C≡C-tAlkyls are only very weakly acidic, while internal acetylenes such as e.g. but-2-yne are not acidic at all due to the absence of an acidic hydrogen atom which is directly bonded to the C≡C entity. The cyclic trimerization reaction proceeds as follows:



1,2,4 1,3,5

The symmetric 1,3,5-trisubstituted benzene is disfavoured for more bulkier binaphtol or bisphenol ligands, i.e. binaphtol and bisphenol ligands having bulky X^1 and X^2 groups. Consequently, the ratio of 1,2,4-trisubstituted benzene to its 1,3,5-isomer can be controlled by the nature of the X^1 and X^2 groups bonded to the metal atom.

The invention is further illustrated by the following examples, however without restricting the invention to these specific embodiments.

Examples

All experiments for preparing the chelating alkoxide titanium and zirconium compounds were performed in an argon atmosphere using Schlenk type glassware or in a Braun single station dry-box equipped with a -40 °C fridge under a nitrogen atmosphere (Schlenk and Braun are trade marks).

Nuclear Magnetic Resonance (NMR) spectra were recorded on Varian XL-200, Varian VXR-300 or Bruker-500 MHz spectrometers (Varian and Bruker are trade marks). Chemical shifts (δ) are reported in parts per million and referenced to the residual protons in deuterated solvents. Coupling constants J_{AB} are reported in hertz (Hz). Solvents were P.A. grade and were dried over sodium wire, then distilled from the appropriate drying reagent (sodium benzophenone ketyl for ether and THF, sodium for hexane and toluene) under argon prior to use. Deuterated solvents were dried over 4 ängstrom molecular sieves.

Binaphtol and bisphenol ligands were prepared according to methods described in J. Org. Chem. **1981**, 46, 393; Bull. Chem. Soc. Japan **1988**, 61, 2975; Tet. Lett. **1983**, 24, 5611; J. Chem. Soc., C **1971**, 1750 and J. Org. Chem. **1983**, 48, 4948.

$Zr(CH_2Ph)_2Cl_2$ and $M(CH_2Ph)_4$ (M=Ti, Zr) were prepared according to the methods described in J. Organomet. Chem. **1981**, 205, 319 and J. Organomet. Chem. **1971**, 26, 357.

Melting points of the polymers were determined by Differential Scanning Calorimetry (DSC).

Example 1

$(1,1'\text{-}\{2,2',3,3'\text{-}OC_{10}H_5SiMe_3\}_2)ZrCl_2$ -which corresponds to the compound of formula (V) wherein M=Zr, $R^a=R^b=R^c$=methyl and $X^1=X^2$=Cl- was prepared as follows.

0.494 g (1.18 mmol) $Zr(CH_2Ph)_2Cl_2$ was dissolved in 5 ml toluene at 25 °C. To this solution was added 0.338 g (1.18 mmol) 3,3'-bis(trimethylsilyl)-1,1'-bi-2,2'-naphtol dissolved in 5 ml toluene. After stirring for 16 hours at 20 °C the toluene was removed in vacuo and the red-brown powder was washed with hexane. Recrystallization from an ether/hexane 1:1 mixture at -40 °C afforded a yellow powder. Yield: 0.383 g, corresponding to 73%.

^1H NMR (C_6D_6, 25 °C): δ 8.10 (s, 2H); 7.8-7.7 (d, 2H); 7.2-6.95 (m, 4H); 6.86-6.75 (m, 2H); 0.70 (s, 18H, Si$\underline{Me_3}$)
^{13}C NMR (C_6D_6): δ 158.1; 135.7; 129.6; 128.4; 128.3; 128.2; 125.7; 124.7; 123.6; 111.4; -0.58 (Si$\underline{Me_3}$)

Analysis for $C_{26}H_{28}O_2Si_2Cl_2Zr$:					
Calculated:	C, 52.86;	H, 4.78;	Si, 9.51;	Cl, 12.00;	Zr, 15.44
Found :	C, 53.12;	H, 5.04;	Si, 9.20;	Cl, 11.86;	Zr, 15.30

Example 2

(1,1'-{2,2',3,3'-$OC_{10}H_5SiMePh_2$}$_2$)$ZrCl_2$ -which corresponds to the compound of formula (V) wherein M=Zr, R^a=methyl, R^b=R^c=phenyl and X^1=X^2=Cl- was prepared in a similar manner as described in Example 1.

^{1}H NMR (C_6D_6, 25°C): δ 7.75 (br, 6H); 7.62 (d, 2H); 7.52 (d, 2H); 7.43 (m, 6H); 7.27 (m, 6H); 7.17 (t, 2H); 7.06 (t, 2H); 6.73 (d, 2H); 1.17 (s, 6H, Me)

Analysis for $C_{48}H_{38}O_2Si_2Cl_2Zr$:					
Calculated:	C, 65.76;	H, 5.08;	Si, 6.15;	Cl, 7.76;	Zr, 9.99
Found :	C, 65.58;	H, 5.14;	Si, 6.19;	Cl, 8.00;	Zr, 10.10

Example 3

(1,1'-{2,2',3,3'-$OC_{10}H_5SiPh_3$}$_2$)$ZrCl_2$ -which corresponds to the compound of formula (V) wherein M=Zr, R^a=R^b=R^c=phenyl and X^1=X^2=Cl- was prepared in a similar manner as described in Example 1.

^{1}H NMR (C_6D_6/d^8-THF, 25 °C): δ 8.07 (s, 2H); 8.0 (m, 12H); 7.35 (d, 2H); 7.25-7.15 (m, 18H); 7.35 (d, 2H); 6.86 (t, 2H, 7.7 Hz); 6.75 (t, 2H, 7.7 Hz)

^{13}C NMR (C_6D_6): δ 160.2; 142.1; 137.1; 137.0; 135.5; 129.9; 129.8; 128.8; 127.4; 126.8; 124.5; 124.0; 117.9

Analysis for $C_{56}H_{40}O_2Si_2Cl_2Zr$:					
Calculated:	C, 69.47;	H, 4.86;	Si, 5.41;	Cl, 6.48;	Zr, 8.79
Found :	C, 69.22;	H, 5.04;	Si, 5.30;	Cl, 6.69;	Zr, 8.61

Example 4

(1,1'-{2,2',3,3'-$OC_{10}H_5SiMe_3$}$_2$)$Ti(CH_2Ph)_2$ -which corresponds to the compound of formula (V) wherein M=Ti, R^a=R^b=R^c=methyl and X^1-X^2=benzyl- was prepared as follows.

To 0.153 g (0.371 mmol) $Ti(CH_2Ph)_4$ dissolved in 10 ml toluene and cooled to -40 °C was added 0.16 g (0.372 mmol) $(HOC_{10}H_5SiMe_3)_2$. The solution was allowed to warm to 20 °C with stirring and was stirred at this temperature for 15 hours. The toluene was removed in vacuum to afford a red oil, which was recrystallized to give the solid product.

^{1}H NMR (C_6D_6, 25 °C): δ 8.17 (s, 2H); 7.2-6.8 (m); 2.87 (2H, AB, CH2); 2.35 (AB, 2H, CH_2); 0.48 (s, 18H, $SiMe_3$)

Example 5

(1,1'-{2,2',3,3'-$OC_{10}H_5SiMePh_2$}$_2$)$Zr(CH_2Ph)_2$ -which corresponds to the compound of formula (V) wherein M=Zr, R^a=methyl, R^b=R^c=phenyl and X^1=X^2=benzyl- was prepared analogous to Example 4 using $Zr(CH_2Ph)_4$.

Example 6

(1,1'-{2,2',3,3'-$OC_{10}H_5SiPh_3$}$_2$)$Ti(CH_2Ph)_2$ -which corresponds to the compound of formula (V) wherein M=Ti, R^a=R^b=R^c=phenyl and X^1=X^2=benzyl- was prepared analogous to Example 4.

^{1}H NMR (C_6D_6, 25 °C): δ 8.33 (s, 2H); 8.0-7.92 (m, 12H); 7.2-6.8 (m + C_6D_5H); 6.75 (m, 4H); 6.45 (m, 4H); 1.4 (AB, J_{AB} = 11 Hz, 2H, CH_2); 1.05 (AB, J_{AB} = 11 Hz, 2H, CH_2)

Analysis for $C_{70}H_{54}O_2Si_2Ti$:			
Calculated:	C, 81.53;	H, 5.28;	Ti, 4.64
Found :	C, 81.24;	H, 5.41;	Ti, 4.75

Example 7

(1,1'-{2,2',3,3'-$OC_{10}H_5SiPh_3$}$_2$)$ZrMe_2(ether)_2$ -which corresponds to the compound of formula (V) wherein M=Zr, R^a=R^b=R^c=phenyl and X^1=X^2=methyl- was prepared as follows. 0.896 g (0.83 mmol) ($C_{110}H_5OSiPh_3$)$_2ZrCl_2$.toluene was suspended in 60 ml ether in a small Schlenk tube. This was cooled to -40 °C and 2 equivalents MeLi (1.04 ml of 1.6 M solution) in ether were added dropwise. After 10 minutes the orange suspension became a clear yellow solution and then began to turn cloudy. The solution was filtered, concentrated under vacuum and crystallized at -40°C to give a white crystalline solid.

^1H NMR (C_6D_6, 25 °C): δ 8.28 (s, 2H); 7.92 (m); 7.53 (m); 7.16 (m); 6.97 (m); 3.14 (q, 8H, ether); 0.78 (t, 12H, ether); -0.136 (s, 6H, Me) 6.75 (t, 2H, 7.7 Hz)

^{13}C NMR (C_6D_6): δ 159.86; 142.0 (d, 149 Hz); 138.2; 136.2; 129.3; 127.1; 125.8; 123.3; 118.2; naphtyl and phenyl resonances: 66.1 (t, 141 Hz, ether); 46.04 (q, 118 Hz, Me); 14.22 (q, 129 Hz, ether)

Analysis for $C_{56}H_{40}O_2Si_2Cl_2Zr$:					
Calculated:	C, 74.48;	H, 5.21;	Zr, 8.33		
Found :	C, 74.75;	H, 5.32;	Zr, 8.60;	Li, 0.0;	Cl<0.2

Example 8

(1,1'-{2,2',3,3'-$OC_{10}H_5SiPh_3$}$_2$)$Zr(CH_2Ph)_2$ -which corresponds to the compound of formula (V) wherein M=Zr, R^a=R^b=R^c=phenyl and X^1=X^2=benzyl- was prepared as follows.

To 0.795 g (1.74 mmol) $Zr(CH_2Ph)_4$ dissolved in 30 ml toluene was added 1.4 g (1.74 mmol) 3,3'-bis(triphenylsilyl)-1,1'-bi-2,2'-naphtol. After stirring for 16 hours at 20 °C the toluene was removed in vacuo. The resulting yellow oil was washed with hexane to give a yellow powder. Yield: 1.70 g, corresponding to 91%.

^1H NMR (CD_2Cl_2, 25 °C): δ 8.15 (s, 2H); 7.75 (d, 2H); 7.65 (m, 10H); 7.35 (m, 24H); 6.78 (d, 2H); 6.55 (m, 6H); 5.70 (d, 4H, benzyl H_o); 0.88 (AB, 2H, 9.8 Hz); 0.64 (AB, 2H, 9.8 Hz)

^{13}C NMR (CD_2Cl_2): δ 157.7; 143.9; 138.9; 137.5; 137.1; 134.9; 130.9; 130.0; 129.9; 128.3; 128.1; 127.5; 127.1; 125.9; 124.6; 124.3; 116.1; 68.1 (t, CH_2, J_{CH} = 133 Hz)

Example 9

(1,1'-{2,2',3,3'-$OC_{10}H_5SiPh_3$}$_2$)$Zr(CH_2SiMe_3)_2$ -which corresponds to the compound of formula (V) wherein M=Zr, R^a=R^b=R^c=phenyl and X^1=X^2=methylene trimethyl silyl- was prepared analogous to Example 8.

^1H NMR (CD_2Cl_2, 25 °C): δ 8.35 (s, 2H); 8.0-7.92 (m, 12H); 7.2-6.8 (m + C_6D_5H); 7.15 (d, 2H); 0.5 (AB, 2H, CH_2); -0.50 (AB, 2H, CH_2); -0.4 (s, 18H, $SiMe_3$)

^{13}C NMR (CD_2Cl_2): δ 156.0; 142.9; 137.3; 137.0; 130.1; 130.0; 128.8; 128.7; 128.4; 128.0; 127.0; 126.1; 124.4; 117.2 (phetyl and phenyl resonances); 67.6 (CH_2); 1.3 ($SiMe_3$)

Example 10

In this example the use of several chelating alkoxide titanium and zirconium catalysts in the polymerization of ethene and propene is illustrated.

Preparation of 2,2'-S(4-Me,6-$tBuC_6H_2O$)$_2Ti(CH_2Ph)_2$(Cat 1)

This compound corresponds to Formula (I) with X^1=X^2=benzyl having as the alkoxide ligand the ligand of formula (II), wherein n=1, Y=-S-, R^1=R^2=tertiary butyl and R^3=R^4=methyl.

0.21 g 2,2'-S(4-Me,6-tBuC_6H_2OH)$_2$ dissolved in 2 ml toluene was added to a cooled (-20 °C) solution of 0.24 g (0.583 mmol) Ti(CH_2Ph)$_4$ in 3 ml toluene/5 ml hexane. The red purple solution was stirred for 1 hour at 20 °C and the solvent was removed under vacuum. Extraction with hexane gave a dark red, very hexane soluble, slightly oily product. Recrystallization from hexane yielded analytically pure Cat 1.

Preparation of 2,2'-CH_2(4-Et,6-tBuC_6H_2O)$_2$Ti(CH_2Ph)$_2$(Cat 2)

This compound corresponds to Formula (I) with X^1=X^2=benzyl having as the alkoxide ligand the ligand of formula (II), wherein n=1, Y=methylene, R^1=R^2=tertiary butyl and R^3=R^4=ethyl.

81 mg (0.20 mmol) Ti(CH_2Ph)$_4$ in 5 ml hexane was cooled to -40 °C and then added to a suspension of 72 mg (0.20 mmol) of 2,2'-bis(3-t-butyl-5-ethylphenol) in 5 ml hexane, also cooled to -40 °C. After addition at -40 °C the suspension was allowed to warm slowly to 20 °C. After stirring for 2 hours at 20 °C the resulting red coloured solution stripped under vacuum to give a red foam. Crystallization of a concentrated hexane solution at -40 °C gave micro-crystalline Cat 2.

Preparation of 2,2'-(4-OMe,6-tBuC_6H_2O)$_2$Ti(CH_2Ph)$_2$(Cat 3)

This compound corresponds to Formula (I) with X^1=X^2=benzyl having as the alkoxide ligand the ligand of formula (II), wherein n=0, R^1=R^2=tertiary butyl and R^3=R^4=methoxy.

114 mg (0.275 mmol) Ti(CH_2Ph)$_4$ in 5 ml toluene was added to a suspension of 99 mg (0.275 mmol) 2,2'-bis(3-t-butyl-5-methoxyphenol) in 5 ml toluene. After stirring for 16 hours at 20 °C the toluene was removed in vacuo. This afforded a purple coloured oil which could be crystallized from hexane or ether at -40 °C to give red block-like crystals.

Polymerization experiments

In table 1 ethene polymerization results for several titanium and zirconium compounds are listed. In each polymerization experiments the following conditions were applied:

- ethylene pressure: 3 bar
- polymerization temperature: 20 °C, except for the catalyst of Example 4, Cat 1 and Cat 3, where the polymerization temperature was 40 °C
- 0.02 mmol catalyst
- 5 mmol methylaluminoxane as a 10% solution in toluene
- 200 ml toluene
- polymerization time: 15-30 minutes, except for Cat 3, where the polymerization time was 1.5 hours

Table 1

Ethene polymerization					
Catalyst of	Rate (kg/g M/hr)	M_w	M_n	PD	m.p. (°C)
Example 1	8.5	$2x10^5$	8300	24	125
Example 2	2.3	$3.6x10^5$	24000	15	120
Example 3	3.3				133
Example 4	2.0	$4.2x10^5$	39000	10.5	133
Example 5	9.2				133
Example 9	0.53				
Cat 1	10.4	$3.4x10^5$	50000	7.0	117
Cat 2	2.8				
Cat 3	0.38				

In the above table M_w is weight average molecular weight, M_n is number molecular weight and PD stands

for polydispersity and is equal to M_w/M_n. Molecular weight data were determined by GPC. The melting point (m.p.) of the polyethylene obtained was determined by DSC.

Example 11

The catalyst of Example 1 was also used for the polymerization of propene. At a polymerization temperature of 45 °C, a propene pressure of 6 bar and a polymerization time of 60 minutes -all other conditions are equal to those applied during ethene polymerization- the following date were obtained.

Rate : 0.43 (kg/g Zr/hr)
M_w : $1.2x10^5$
M_n : 7600
PD : 15.8

Example 12

To 0.02 mmol of the catalyst of Example 5 in 200 ml toluene were added 200 equivalents of HC≡CR at 20 °C, with R as defined in table 2. The trimerization was complete within 5 minutes at 20 °C. The same experiment was performed using the catalyst of Example 8.

The results are listed in table 2.

Table 2

Cyclic trimerization of HC≡CR		
Catalyst of	R	Ratio 1,2,4 : 1,3,5
Example 5	$SiMe_3$	1 : 1
(R^1=R^2=$SiMePh_2$)	phenyl	1 : 1
	p-tolyl	1 : 1
Example 8	$SiMe_3$	4 : 1
(R^1=R^2=$SiPh_3$)	phenyl	4 : 1
	p-tolyl	4 : 1

From table 2 it is clear that the use of more bulky substituents R^1 and R^2 ($SiPh_3$ as compared to $SiMePh_2$) disfavour the formation of the 1,3,5-trisubstituted benzene.

Example 13

1-hexene polymerisation

Ca. 2 x 10^{-5} mol catalyst was dissolved in 5 ml 1-hexene at 20 °C in the drybox. A ca. 100 fold excess of MAO was added as a solution in 3 ml toluene. The homogeneous solution formed was stirred for 16 h at 20 °C. The reaction vessel was then removed from the drybox and MeOH and then 1 M HCl added to destroy excess MAO. The toluene solution was decanted and evaporated. Identification of polyhexene was performed by ^1H and ^{13}C NMR spectroscopy, and GPC analysis. The molar mass was determined by GPC. For NMR analysis the polymer was dissolved in $CDCl_3$. The endgroups were identified by APT experiments and fully coupled ^{13}C NMR. DSC analysis (-40 °C ▪ 100 °C) shows no T_g or T_m.

Table 3 lists the results of the hexene polymerization runs with reference to the catalysts mentioned hereinbefore.

Table 3

1-hexene polymerization			
Catalyst	Results		
Catalyst 3	oligomers	Mw = 290	P.D. = 1.21
Catalyst 1	polyhexene	Mw = 19000	P.D. = 1.71
Example 2	polyhexene	Mw = 670000	P.D. = 2.23
Example 5	polyhexene	-	
Example 8	polyhexene	-	
Example 6	oligomers	-	

1,3-butadiene polymerization

A 25 ml autoclave was charged with 2×10^{-5} mol catalyst, a 100 fold excess of MAO and 15 ml toluene. It was pressurized with 1.5 bar butadiene at 20 °C. After 3 h the autoclave was opened and the excess MAO destroyed by addition MeOH and 1 M HCl. Decanting the organic layer and evaporating the solvents yielded polybutadiene as a rubber-like polymer. The structure was identified by ^1H and ^{13}C NMR spectroscopy. The ratio between 1,2-methylene and 1,4-cis/trans units was determined by ^1H NMR spectroscopy. To dissolve the polymer it was refluxed in $C_2D_2Cl_4$ for 1 h under an inert atmosphere. 1,2-methylene units resonate at 4.8 and 1.3 ppm, 1,4-trans units at 1.98 and 5.4 ppm, and 1,4-cis units at 5.32 and 2.03 ppm. The ratio can be calculated from the integral of the individual peaks. E.R. Santee, Jr., R. Chang and M. Morton Polymer Lett. Ed. 1973, 11, 453.

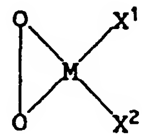
Table 4 lists the results of the butadiene polymerization runs referring to the catalysts mentioned before.

Table 4

Butadiene polymerization		
Catalyst	Results	
Catalyst 3	polybutadiene,	mixture of 30% 1,2-vinyl, cis/trans-1,4
Catalyst 1	polybutadiene	-
Example 2	polybutadiene	no 1,2-vinyl, cis/trans-1,4
Example 5	polybutadiene	-
Example 8	polybutadiene	no 1,2-vinyl, 50/50 cis/trans-1,4
Example 6	polybutadiene	7% 1,2-vinyl, 7% trans-1,4, 81% cis-1,4

Claims

1. A process for the polymerization or oligomerization of olefinically or acetylenically unsaturated hydrocarbons in the presence of a homogeneous catalyst characterized in that the latter is a compound of general formula (I)

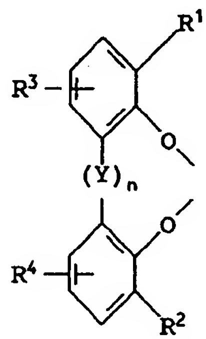


(I)

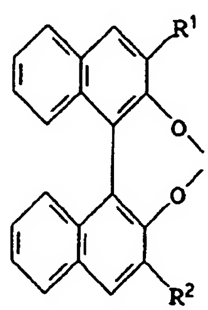
wherein:

- M is Ti or Zr;
- X^1 and X^2 independently represent halogen, an optionally substituted aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms, a silyl group or an alkoxy group of general formula -OR' with R' being an aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms;
-

represents a chelating alkoxide ligand of general formula (II) or (III):



(II)



(III)

wherein:

- R^1 and R^2 independently represent a sterically hindering alkyl group or an alkoxy group of general formula OR' with R' as previously defined, or a silyl group of general formula $SiR^aR^bR^c$ with R^a, R^b and R^c independently representing a lower alkyl group, an aryl group, an arylalkyl group or an alkylaryl group;
- R^3 and R^4 independently represent hydrogen, an optionally substituted aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms, a silyl group or an alkoxy group of general formula OR' with R' as previously defined;
- Y is a divalent bridging group selected from the group consisting of methylene, ethylene, -S- and -O-; and
- n is 0 or 1,

2. A process according to claim 1, wherein the unsaturated hydrocarbon is ethene or propene and the polymerization is effected in the presence of an organo aluminium cocatalyst.

3. A process according to claim 1, comprising the cyclic trimerization of a terminal acetylene having the formula (IV):

$$H\text{-}C\equiv C\text{-}R \qquad (IV)$$

wherein R represents a hydrocarbyl silyl group, an optionally substituted aryl group or an alkyl group of 1 to 20 carbon atoms other than a tertiary alkyl.

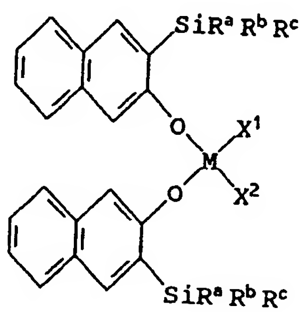
4. A process according to any one of claims 1 to 3, wherein X^1 and X^2 in formula (I) are the same and selected from the group consisting of halogen, alkylene trialkyl silyl, aryl, alkylaryl, arylalkyl and lower alkyl.

5. A process according to any one of claims 1 to 4, wherein R^1 and R^2 are the same and represent a sterically hindering alkyl group of 4 to 10 carbon atoms.

6. A process according to any one of claims 1 to 5, wherein R^3 and R^4 are located on the meta-position in relation to R^1 and R^2 respectively.

7. A process according to claim 6, wherein R^3 and R^4 are the same and represent methoxy, methyl or ethyl.

8. Novel compound of general formula (V):



(V)

wherein:
- M is Ti or Zr;
- X^1 and X^2 independently represent halogen, an optionally substituted aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms, a silyl group or an alkoxy group of general formula -OR' with R' being an aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms; and
- R^a, R^b and R^c independently represent a lower alkyl group, an aryl group, an arylalkyl group or an alkylaryl group.

9. Compound according to claim 8, wherein X^1 and X^2 are selected from the group consisting of chlorine, benzyl, methylene trimethyl silyl and methyl.

10. Compound according to any one of claims 8 to 9, wherein R^a, R^b and R^c are selected from methyl and phenyl.

11. Compound according to any one of claims 8 to 10, wherein: M-Zr or Ti, $R^a=R^b=R^c$=independently methyl or phenyl and $X^1=X^2$=Cl or benzyl or methyl.

12. Compound according to any one of claims 8 to 10, wherein: M=Zr, $R^a=R^b=R^c$=phenyl and $X^1=X^2$=methylene trimethyl silyl.